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⑤④ **Liquid fuels containing corrosion inhibitors, and inhibitor concentrates.**

⑤⑦ Corrosion caused by gasohol or alcohol motor fuels is inhibited by the addition of a corrosion inhibiting amount of the combination of (A) a polymer of one or more C<sub>16</sub> to C<sub>18</sub> polyunsaturated aliphatic monocarboxylic acid (e.g. linoleic dimer and/or trimer) and (B) a hindered phenol antioxidant, e.g. 2,6-di-( $\alpha$ -methylbenzyl)-4-nonyl phenol.

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LIQUID FUELS CONTAINING CORROSION  
INHIBITORS, AND INHIBITOR CONCENTRATES

5           In the past metal corrosion caused by conventional  
motor fuels such as gasoline was not much of a problem  
because such hydrocarbon fuels are inherently non-  
corrosive. However, with the advent of fuels containing  
alcohols such as gasohol or straight alcohol fuels,  
10 corrosion has become a major problem because such fuels  
are corrosive. It has been reported that this corrosion  
is due to the presence of acidic contaminants in such  
fuels such as formic acid. It is almost impossible to  
avoid such contaminants because they occur in fuel grade  
15 alcohols and are also formed in storage as normal alcohol  
oxidation products.

          It is known from U.S. 4,305,730 that polymerized  
linoleic acid, especially trimer, is an effective  
corrosion inhibitor for alcohol-type motor fuels. It has  
20 now been discovered that the corrosion inhibiting  
properties of such polymerized polyunsaturated aliphatic  
monocarboxylic acids are improved by use of the co-  
additives described herein.

According to the present invention metal corrosion caused by alcohol-type motor fuels is inhibited by adding to the fuel a combination of (A) polymerized polyunsaturated aliphatic monocarboxylic acid and (B) a sterically hindered phenol.

The invention provides a liquid fuel adapted for use in an internal combustion engine said fuel comprising from 5 to 100 weight percent of one or more alcohols, from 0 to 95 weight percent gasoline and a corrosion inhibiting amount of the combination of (A) a polymer of one or more  $C_{16}$  to  $C_{18}$  polyunsaturated aliphatic monocarboxylic acids and (B) at least one sterically hindered phenol.

The additive combination of this invention can be beneficial in any engine fuel containing or consisting of an oxygenate. Such fuels include gasoline-alcohol mixtures referred to as "gasohol" as well as straight alcohol fuels. Useful alcohols are methanol, ethanol, n-propanol, isopropanol, isobutanol and the like. Gasohols usually contain about 2 to 30 volume percent alcohol. The most prevalent alcohols are methanol and ethanol. At concentrations above 10 volume percent phase separation problems are encountered especially in the presence of water.

Phase separation can be minimised by including co-solvents in the gasohol such as ethers, ketones, esters and the like. An especially useful co-solvent is methyl tert-butyl ether which also serves to increase octane  
5 value.

The additive combination may be used at a concentration which provides the required amount of corrosion protection. A useful range is about 1 to 5000 parts per million (ppm). A more preferred range  
10 is about 5 to 2000 ppm and the most preferred concentration is 10 to 500 ppm.

Component A is a polymer of one or more 16 to 18 carbon polyunsaturated aliphatic monocarboxylic acids. Examples of these are linolenic acid and linolenic  
15 acid including mixtures thereof. The polymers comprise mainly dimers and trimers of the polyunsaturated acids. Suitable polymers of linoleic acid are available commercially. Mixtures high in trimer content are most preferred.

20 Component B of the combination is a hindered phenol. This includes any fuel (i.e. gasohol or alcohol fuels) soluble phenol having at least one bulky substituent ortho to a phenolic hydroxyl group.

Representative bulky substituents are secondary and tertiary alkyl (including cycloalkyl and alkyl (cycloalkyl) or aralkyl groups.

More preferably the hindered phenols are substituted in both positions ortho to a phenolic hydroxyl group with a secondary or tertiary alkyl or aralkyl group. Such phenols include

- 2,6-di-sec-butylphenol
- 2,6-diisopropyl phenol
- 10 2,6-di-tert-butylphenol
- 2,6-di-sec-octylphenol
- 2-tert-butyl-6-( $\alpha$ -methylbenzyl)phenol
- 2-isopropyl-6-( $\alpha$ ,  $\alpha$ -dimethylbenzyl)phenol
- 2,6-di-( $\alpha$ -methylbenzyl)phenol
- 15 2,6-di-( $\alpha$ ,  $\alpha$ -dimethylbenzyl)phenol and the like.

In a highly preferred embodiment the hindered phenols are also substituted in the para position with an alkyl group containing 1 to about 20 carbon atoms.

Examples of these hindered phenols are

- 20 2,6-di-tert-butyl-4-methyl phenol
- 2,6-di-tert-butyl-4-ethyl phenol
- 2,6-di-tert-butyl-4-(n-butyl) phenol
- 2,4,6-tri-tert-butyl phenol

2,6-di-tert-butyl-4-(sec-octyl) phenol  
2,6-di-tert-butyl-4-(sec-eisoyl) phenol  
2,6-diisopropyl-4-methylphenol  
2,4,6-tri-sec-butyl phenol and the like.

5 In a still more preferred embodiment the hindered phenol is a 2,6-di-( $\alpha$ -methylbenzyl)-4-C<sub>1-20</sub> alkyl phenol. These include

2,6-di-( $\alpha$ -methylbenzyl)-4-methyl phenol  
2,6-di-( $\alpha$ -methylbenzyl)-4-ethyl phenol  
10 2,6-di-( $\alpha$ -methylbenzyl)-4-tert-butyl phenol  
2,6-di-( $\alpha$ -methylbenzyl)-4-(n-butyl) phenol  
2,6-di-( $\alpha$ -methylbenzyl)-4-(sec-octyl) phenol  
2,6-di-( $\alpha$ -methylbenzyl)-4-nonylphenol  
2,6-di-( $\alpha$ -methylbenzyl)-4-dodecylphenol  
15 2,6-di-( $\alpha$ -methylbenzyl)-4-octadecylphenol  
2,6-di-( $\alpha$ -methylbenzyl)-4-eicosylphenol  
and the like.

Sterically hindered methylenebis phenols are also useful. These include 2,2' methylenebis-(4-alkyl-6-  
20 tert-alkyl phenols) and 4,4' methylenebis (2-alkyl-6-tert-alkyl phenols).

Representative examples of these are 2,2-methylenebis  
(4-methyl-6-tert-butyl phenol), 2,2' methylenebis-  
(4,6-di-tert-butyl phenol), 4,4' methylenebis (2,6-  
di-tert-butyl phenol), 4,4'-methylenebis-(2-methyl-  
5 6-tert-butyl phenol) and the like including mixtures  
thereof.

The most preferred hindered phenol is 2,6-di-( $\alpha$ -  
methylbenzyl)-4-nonylphenol. The nonyl group is readily  
available by alkylation with propylene trimer.

10 The weight ratio of component A to component B  
in the combination can vary over a wide range such as  
1 to 10 parts A to 1 to 10 parts B. In a more preferred  
embodiment the weight ratio is about 0.5-5 parts  
component A for each part component B. In a still more  
15 preferred embodiment there are 0.6-4.0 parts component A  
per each part component B. The most preferred ratio  
is 1:1.

Components A and B can be separately added to the  
fuel. More preferably components A and B are pre-  
20 mixed to form a package and this package is added to the  
fuel in an amount sufficient to provide the required  
degree of corrosion protection.

Most preferably components A and B are also pre-mixed with a solvent to make handling and blending easier. Suitable solvents include alcohols (e.g. methanol, ethanol, isopropanol) ketones (acetone, methyl ethyl ketone) esters (tert-butyl acetate) and  
5 ethers (e.g. methyl tert-butyl ether).

Aromatic hydrocarbons are very useful solvents. These include benzene, toluene, xylene and the like. Excellent results have been obtained using xylene.

10 The concentration of the active components A and B in the package can vary widely. For example the active content can range from about 5 weight percent up to the solubility limit of A or B in the solvent. With xylene a total active content of about 5-25 weight  
15 percent is generally used, especially about 10 weight percent.

Tests were conducted to measure the anti-corrosion properties of the additive combination. In the test the corrosion of metal coupons immersed in test fluid  
20 was measured under different test conditions. Aluminium, brass, zinc, lead and copper coupons were used. The coupons were first cleaned with carborundum 40, washed with petroleum ether and oven dried for 10 minutes at 40°C.

- 8 -

Each coupon was weighed and then immersed in 130g of the test fluid in a sealed bottle for the specified time at the specified temperature.

At the end of the test period, the coupons were  
5 removed from the fuel; after loose deposits were removed with a light brush, the coupons were washed and dried as at the start of the test and then reweighed. Any change in coupon weight was recorded. Both gain and loss of weight indicate corrosion.

10 The corrosion was characterised by two modes, either weight loss by loss of metal or weight gain due to deposition of corrosion products, in the tests carried out below, visual examination of the coupons after test indicated that the two modes were mutually exclusive.

15 The first series of tests was conducted in various alcohol type fuels containing 100 ppm of the equal weight combination of linoleic acid polymer (mainly trimer) and 2,6-di-( $\alpha$ -methylbenzyl)-4-nonylphenol.

- 9 -

In this test series the temperature was ambient and immersion time 6 weeks. Results are given in the following table in terms of mg weight gain or loss. The value in parenthesis is the result without any inhibitor.

5

TABLE 1

<u>Metal</u>	<u>Test Fuel</u>		
	<u>Gasohol</u> <sup>1</sup>	<u>Wet Gasohol</u> <sup>2</sup>	<u>Wet Methanol</u> <sup>3</sup>
Aluminium	0.0 (+0.3)	+0.5 (+0.5)	0 (-0.8)
10 Brass	+0.4 (-0.5)	-0.3 (-0.9)	-0.1 (-1.0)
Zinc	+0.1 (-0.2)	+0.1 (+0.2)	+0.1 (-1.1)
Lead	+0.9 (+0.1)	-0.4 (-0.1)	-224 (-408)
Copper	-0.3 (-0.8)	-0.3 (+0.4)	+0.4 (-1.6)

15 1  
Contained 15 vol percent methanol

2  
Same plus 0.1 weight percent water

3  
Contained 0.1 weight percent water

20

In the next test series the coupons were placed in a bottle containing methanol doped with 100 ppm formic acid and 10 ppm methyl formate to increase test severity. The test additives were equal weight mixture of linoleic acid trimer and various hindered phenols as shown in Table II. Additive concentration was 100 ppm. The bottles with the test coupons were stored two weeks at 40°C. Weight change due to corrosion is shown in Table II.

TABLE II

		<u>Weight Change (mg)</u>		
<u>Hindered Phenol</u>		<u>Brass</u>	<u>Lead</u>	<u>Aluminium</u>
	Blank	+ 0.3	- 347	- 1.8
	y <sup>1</sup>	- 1.7	- 304	- 0.2
15	z <sup>2</sup>	- 0.1	- 294	0

<sup>1</sup>Y is a mixture of tert-butyl phenols comprising mainly 2,6-di-tert butylphenol.

<sup>2</sup>Z is 2,6-di-( $\alpha$ -methylbenzyl)-4-nonylphenol

Further tests were conducted which show the synergistic results obtained with this combination of additives. These tests were in methanol doped with 100 ppm formic acid and 10 ppm methyl formate. The metal coupons were immersed in the fuel and stored two weeks at 40°C.

Additive D was 2,6-di-( $\alpha$ -methylbenzyl)-4-nonyl-phenol. Additive E was linoleic acid trimer. Additive D + E was an equal weight mixture of D and E. Total inhibitor concentration in each test was 300 ppm.

5

TABLE III

<u>Metal</u>	<u>Additive</u>		
	<u>D</u>	<u>E</u>	<u>D + E</u>
Copper	-0.7	+0.3	-0.9
Lead	-525	-454	-340
10 Brass	+0.2	-6.8	+0.6
Aluminium	-0.5	-1.1	+0.6
Zinc	-4.2	-7.8	-1.0

These results show that the combination gives better results than would be expected from the results obtained with each component.

15

In the next test series the fuel was methanol doped with 100 ppm formic acid and 10 ppm methyl formate. The metal coupons were only partially immersed (approx 50%) and the bottles were stored two weeks at 40°C. The additive was a 50/50 mixture of linoleic acid trimer and 2,6-di-( $\alpha$ -methylbenzyl) phenol. Additive concentration was 300 ppm in each samples. Test results are given in Table IV.

20

TABLE IV

		<u>Weight Change (mg)</u>	
<u>Metal</u>	<u>Blank</u>	<u>Inhibited</u>	
Copper	+ 4.1	- 0.2	
5    Lead	- 351	- 263	
Brass	+ 1.7	+ 1.2	
Aluminium	+ 2.9	- 0.2	
Zinc	- 3.3	- 0.8	

The next test was again conducted in gasohol containing 15 vol percent methanol and doped with 100 ppm formic acid and 10 ppm methyl formate. The metal coupons were fully immersed and stored two weeks at 40°C. Additive concentration was 100 ppm. Table V gives the test results with and without the test additive. The test additive was an equal weight mixture of linoleic acid trimer and various hindered phenols as indicated.

TABLE V

		<u>Coupon Weight Change</u>		
<u>Additive</u>	<u>Lead</u>	<u>Aluminium</u>	<u>Copper</u>	
None	-146 mg	+0.9 mg	-8.0 mg	
20    M <sup>1</sup>	-119	+0.5	-4.2	
N <sup>2</sup>	-104	+0.3	-6.2	
O <sup>3</sup>	-112	+0.2	-5.8	

M<sup>1</sup> is linoleic acid trimer plus 2,6-di-( $\alpha$ -methylbenzyl) phenol

25    N<sup>2</sup> is linoleic acid trimer plus mixture of

methylene-bridged 2,6-di-tert-butyl phenol  
and ortho-tert-butyl phenols.

O<sup>3</sup> is linoleic acid trimer plus 2,6-di-tert-  
butyl-4-n-butyl phenol.

5       The test results show that while not equally  
effective on all metals in all fuels, the additive  
combination on average gives very good corrosion  
protection.

CLAIMS

1. A liquid fuel adapted for use in an internal combustion engine, said fuel comprising 5 to 100 weight percent of one or more alcohols, 0 to 95 weight percent gasoline and a corrosion inhibiting amount of a combination of (A) a polymer of one or more C<sub>16</sub> to C<sub>18</sub> polyunsaturated aliphatic monocarboxylic acids and (B) at least one sterically hindered phenol.

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2. A liquid fuel as claimed in claim 1 wherein said polymer of one or more C<sub>16</sub> to C<sub>18</sub> polyunsaturated aliphatic monocarboxylic acids comprises mainly linoleic acid dimer, trimer or mixtures thereof.

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3. A liquid fuel as claimed in claim 1 or claim 2 wherein the or each said hindered phenol is substituted in both positions ortho to the phenolic hydroxyl group with a secondary or tertiary alkyl or aralkyl group.

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4. A liquid fuel as claimed in claim 3 wherein said phenol is a 2,6-di-( $\alpha$ -methylbenzyl)-4-C<sub>1-20</sub>-alkyl-phenol.

5. A liquid fuel as claimed in claim 4 wherein said phenol is 2,6-di-( $\alpha$ -methylbenzyl)-4-nonylphenol.

6. A liquid fuel as claimed in claim 3 wherein  
5 said phenol is a 2,6-di-tert-butyl-4-C<sub>1-20</sub> alkyl phenol.

7. A liquid fuel as claimed in claim 6 wherein said phenol is 2,6-di-tert-butyl-4-butylphenol.

10 8. A liquid fuel as claimed in claim 6 wherein said phenol is 2,6-di-tert-butyl-4-methylphenol.

9. A liquid fuel as claimed in claim 3 wherein said phenol is 4,4'-methylenebis-2,6-di-tert-butylphenol).

15

10. A corrosion inhibitor concentrate comprising a solvent containing at least 5% by weight of a combination of (A) a polymer of one or more C<sub>16</sub> to C<sub>18</sub> polyunsaturated aliphatic monocarboxylic acids and (B) at least one  
20 sterically hindered phenol.



European Patent  
Office

# EUROPEAN SEARCH REPORT

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Application number

EP 83 30 1021

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
A	US-A-3 346 355 (G.W. ECKERT) * Claims 1-3 *	1,2,10	C 10 L 1/18 C 10 L 1/02
A	GB-A-1 053 065 (MOBIL OIL) * Claim 1 *	1,2,10	
A	FR-A-1 558 064 (ATLANTIC RICHFIELD CO.) * Claim *	1,2	
D,A	US-A-4 305 730 (M.E. DAVIS) * Claims 1-9 *	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )
			C 10 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-09-1983	Examiner MICHIELS P.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	